Scandium-Catalyzed Carbon–Carbon Bond Formations Using α-Organosulfanyl and Organoselanyl-α-fluoroacetic Acid Derivatives

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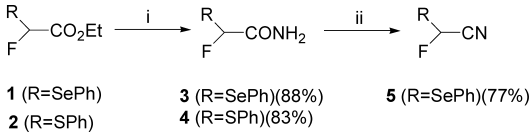
The scandium-catalyzed reactions of α-organosulfanyl and organoselanyl-α-fluoroacetates 1—2, acetamides 3—4 and acetonitrile 5 with soft nucleophiles proceeded to give the products 6a—b, 7a—c, 8a—c, 9a—e in good to high yields. We also successfully performed the scandium-catalyzed intramolecular cyclization reactions and obtained the unique 5-methylene-2-oxotetrahydropyrans 16—17.

Key words scandium; catalytic reaction; α-organosulfanyl carbenium ion; α-organoselanyl carbenium ion

Recently, we have reported a Lewis acid-catalyzed generation and reaction of α-organosulfanyl and α-organoselanyl carbenium ions using ethyl α-fluoroacetates.[1)] The carbon–fluoride bond of the α-organosulfanyl and organoselanyl-α-fluoroacetates were selectively cleaved by Lewis acids such as lanthanoide metals and utilized for the C–C and C–heteroatom bond formation reactions. α-Fluoroacetates are much superior to the corresponding α-chloro[2—4)] and α-bromo derivatives[5)] in respect of the stability and handling of the starting materials. Furthermore, α-fluoroacetates are highly reactive to the Lewis acids and selectively generated the α-selanyl and sulfanyl carbenium ions, while the α-chloro derivatives gave rise to the formation of bis (organoselanyl) acetals and other unknown compounds. In this report, we describe the Lewis acid-catalyzed reactions of α-sulfanyl and selanylacetonitrile and acetamides derived from the ethyl α-fluoroacetate with some nucleophiles and the intramolecular cyclization reactions.

First, we prepared some α-fluoroacetic acid derivatives as shown in Chart 1. α-Phenylsulfanyl and α-phenylselanylacetamides **3** and **4** were obtained by the reactions with 28% aqueous NH_3. The transformation to the nitrile **5** was successfully carried out with the usual dehydrating agent, polyphosphoric acid trimethylsilyl ester (PPSE)[6—8)]; however, the corresponding sulfur analog was not obtained by the same method.

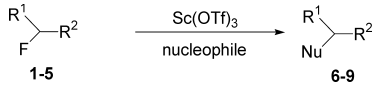
In the previous report, we showed that some scandium-catalyzed reactions of ethyl α-fluoroacetates **1** and **2** with the soft nucleophiles successfully proceeded in the presence of 5 mol% of scandium triflate.[1)] The representative examples are shown in entries 1—5 of Table 1. The carbon nucleophiles such as allyltrimethylsilane and the silyl enol ether and the phenylsulfanyltrimethylsilane exclusively provided the products **6a**—**b** and **7a**—**c** in high yields. We also performed the reactions of α-fluoroacetamides **3** and **4** and the results are shown in entries 6—8 of Table 1. Most of the experiments were performed in 1,2-dichloroethane or nitromethane at room temperature or reflux conditions. It needed 5 mol% of Lewis acid to complete the allylation of acet-



Reagents: i, 28%NH_3/EtOH/15min; ii, polyphosphoric acid trimethylsilyl ester/$ClCH_2CH_2Cl$/83°C/12h

Chart 1. Preparations of α-Phenylsulfanyl and Phenylselanyl-Fluoroacetamides and Fluoroacetonitriles

Table 1. Scandium-Catalyzed Reactions of α-Fluoroacetic Acid Derivatives **1**—**5**



Entry	R^1	R^2	Condition[a)]	Product (Nu) (% yield)
1	PhSe	CO_2Et	Allyltrimethylsilane/83 °C/3 h	**6a** (allyl) (87)
2	PhSe	CO_2Et	$CH_2=C(OSiMe_3)Ph$/rt/4 h	**6b** (CH_2COPh) (78)
3	PhS	CO_2Et	Allyltrimethylsilane/83 °C/3 h	**7a** (allyl) (86)
4	PhS	CO_2Et	$CH_2=C(OSiMe_3)Ph$/rt/4 h	**7b** (CH_2COPh) (89)
5	PhS	CO_2Et	$PhSSiMe_3$/rt/4 h	**7c** (SPh) (95)
6	PhS	$CONH_2$	Allyltrimethylsilane/83 °C/3 h	**8a** (allyl) (82)
7	PhS	$CONH_2$	$CH_2=C(OSiMe_3)Ph$/rt/4 h	**8b** (CH_2COPh) (30)
8	PhSe	$CONH_2$	Allyltrimethylsilane/83 °C/12 h	**8c** (allyl) (82)
9	PhSe	CN	$CH_2=C(OSiMe_3)Ph$/20 °C/10 min	**9a** (CH_2COPh) (75)
10	PhSe	CN	$Me_2C=CH(OSiMe_3)$/20 °C/30 min	**9b** (CMe_2CHO) (81)
11	PhSe	CN	$CH_2=C(OSiMe_3)t$-Bu/20 °C/10 min	**9c** (CH_2COt-Bu) (85)
12	PhSe	CN	Anisole/83 °C/10 min	**9d** (C_6H_4-*p*-OMe) (43)
13	PhSe	CN	Toluene/83 °C/1 h	**9e** (81)[b)]

a) 5 mol% of $Sc(OTf)_3$ was used in the reactions of ethyl acetate **1**—**5**. *b*) The isomer ratio is $o:p=60:40$.

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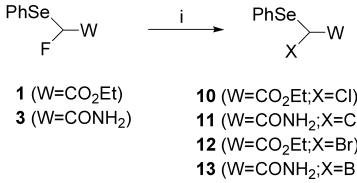

Chart 2. Preparations of Ethyl Halophenylselanylacetate and Halophenylselanylacetamide

amides **8a**, **c**. The reaction with 1-phenyl-1-trimethylsilyloxy ethylene provided the product **8b** in low yield (entry 7). The phenylselanylacetonitrile **5** was a good electrophile for various nucleophile as shown in entries 9—13. Some types of silyl enol ethers gave the corresponding ketones **9a**, **c** and aldehyde **9b** in high yields. The reactions with aromatic compounds also provided **9d**, **e**. However, the regioselectivities of the reactions were very low.

In order to clarify the effect of the fluorine atom in the scandium-catalyzed reactions with nucleophiles, we examined the reactions of α-chloro- and α-bromoacetates and amides **10**—**13**. The chloroester **10** and chloroamide **11** were prepared by our original method using trimethylsilylchloride in nitromethane (Chart 2) because the known methods were not practical for the isolation of the corresponding chlorides. The scandium-catalyzed chlorination of the ester **1** and amide **3** with trimethylsilyl chloride proceeded in high yields over 5 min. The unstable chloroester **10** could be isolated without the usual purification. The bromination also occurred by the almost same method with bromotrimethylsilane. However, the iodination of **1** with iodotrimethylsilane provided a complex mixture. Then, we selected and performed the allylation with allyltrimethylsilane as the representative substrate for the scandium-catalyzed reaction of the phenylselanylacetates **1**, **10**, **12** and amides **3**, **11**, **13** in nitromethane. The allylation of the chloroester **10** with 5 mol% of scandium triflate at refluxing condition for 1 h afforded the product **6a** (5%), chloroester **10** (15%) and ethyl bis(phenylselanyl)acetate (22%), respectively (Chart 3). The reaction of **10** for 2 h gave a complex mixture, while the reaction of fluoroacetate **1** under the same conditions for 10 min exclusively gave the allylated product **6a** in 87% yield, without detection of fluoroester **1** in the reaction mixture. The reaction of α-bromoester **12** over 3 h/reflux gave **6a** in moderate yield. We also examined the reactions of acetamides as shown in Chart 4. The scandium-catalyzed allylation of fluoroamide **3** completely proceeded to give **8c** in 82% yield under the same conditions as 5 mol% of scandium triflate/nitromethane/reflux over 5 min. However, the reaction of chloroacetamide **11** with allyltrimethylsilane over 1 h reflux did not complete and chloride **11** was recovered in 30% yield. The scandium-catalyzed allylation of bromoacetamide **13** did not proceed under both conditions of 2 h/rt and 10 min/refluxing; however, the reaction under 1 h/refluxing effected C–Se bond fission to provide allyl phenyl selenide (62%), accompanied by the allylated product **8c** (28%). From these experiments, the C–Se bond of the bromo derivatives tend to cleave more easily than that of the fluorides. As a whole, the α-fluoroacetates and α-fluoroacetamides were proved to be excellent precursors for the scandium-catalyzed generation of the α-selanyl

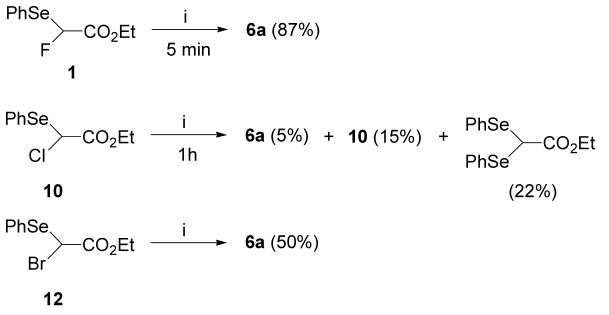

Chart 3. Scandium-Catalyzed Allylation of Ethyl 2-Chloro-2-(phenylselanyl)acetate **11**

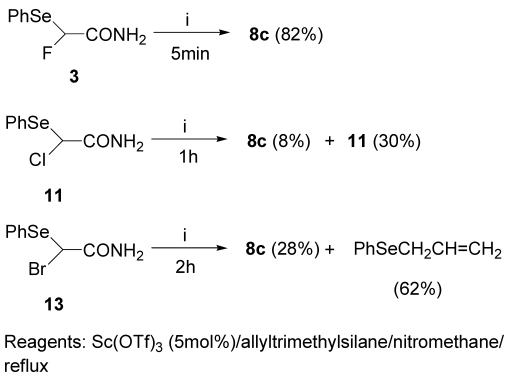

Chart 4. Scandium-Catalyzed Allylation of 2-Chloro- and 2-Bromo-2-(phenylselanyl)acetamide

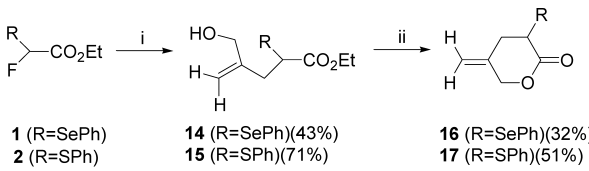

Chart 5. Scandium-Catalyzed Reactions of Ethyl α-Fluoroacetates

carbenium ions with respect to the high-selectivity of the cleavage of the C–F bond and the high-reactivity with nucleophiles.

Next, we tried the intramolecular cyclization reactions using the scandium-catalyzed substitution reaction as shown in Chart 5. Since the allylic trimethylsilanes are found to be a good nucleophile as a scandium-catalyzed reaction using α-fluoroacetates, we performed the reactions with trimethylsilyloxymethyl derivative in the presence of 0.1 eq of $Sc(OTf)_3$. The reaction of **1** provided ethyl 4-(hydroxymethyl)-2-(phenylselanyl)pent-4-enoate (**14**) in 56% yield. The structure of **14** was determined supported by the spectral data, which showed the absorption of the hydroxyl group at ν 3343 cm^{-1} in the IR spectra, and exhibited three kinds of double of doublet due to the 3- and 4-H at δ 2.55 (J=6, 15 Hz), 2.71 (J=10, 15 Hz) and 3.85 (J=6, 10 Hz) ppm and the characteristic *exo*-methylene protons at δ 4.90 and 5.09 ppm in the ^{1}H-NMR spectra, and exhibited the molecular formula as $C_{14}H_{14}O_4Se$ in the mass spectra and the elemental analysis. The phenylsulfanyl acetate **2** also afforded

alcohol **15** in 71% yield. Next, alcohols **14**, **15** were treated with the same Lewis acid in 1,2-dichloroethane under a reflux condition and transformed to the corresponding lactone derivative **16** and **17**. The one-pot transformation from the acetates to the lactones was examined; however, the yields of the lactones could not be improved. 5-Methylene-2-oxatetrahydropyrans are known to be one of the monoterpenes isolated from both the marine sponge, Plakortis zygompha (Laubenfels),[9] and a wild plant, Teucrium marum (Labiatae),[10] which is a powerful lacrimatory essential oil. However, easy accessible methods to these derivatives have not been previously described.[11,12] Our two-step procedure to the 5-methylene-2-oxatetrahydropyrans could be utilized to the more functionalized derivatives by the transformation of the organoselanyl and organosulfanyl functional groups to more useful ones. The formations of the 5-methylenelactam using α-fluoroacetamides **3** and **4** was also examined by the two routes; however, these failed.

In summary, we have described the details of the scandium-catalyzed C–C bond formation of α-fluoroacetic acid esters, amides and nitriles. The carbon–fluoride bond selectively cleaved by the scandium triflate and the generated carbenium ions effectively react with the soft nucleophiles.

Experimental

Melting points were determined on a Yanagimoto micro-melting point apparatus and uncorrected. Elemental analyses were performed by using Micro Corder (MT-6) of J Science Lob. at the Life Science Research Center, Gifu University. ^{1}H- and ^{13}C-NMR spectra were determined with JEOL ECA500 (500 MHz) spectrometer. The ^{19}F-NMR (470.5 MHz) spectra were obtained in $CDCl_3$ with trifluoroacetic acid as the external standard. IR spectra were determined on JASCO FT/IR-460plus infrared spectrometer and are expressed in reciprocal centimeter. Electron impact (EI) mass spectra (MS) were obtained using JMS MS700/GI spectrometer with a direct-insertion probe at an ionization voltage of 70 eV.

Preparation of Ethyl 2-Fluoro-2-(phenylselanyl)acetate (1) $NaBH_4$ (0.49 g, 12.8 mmol) was added portionwise to a EtOH (30.0 ml) solution of diphenyl diselenide (2.00 g, 6.41 mmol). Ethyl chlorofluoroacetate (1.80 g, 12.8 mmol) was added immediately to a colorless solution (if the color of the reaction mixture became yellow, a small amount of $NaBH_4$ was added to it upto the mixture was colorless). The whole was stirred for 10 min at room temperature and poured into water (100 ml). The organic layer was separated and the aqueous layer was extracted with ether. The combined organic layer was dried over $MgSO_4$. The solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel eluting with EtOAc–*n*-hexane (1 : 10) to give ethyl 2-fluoro-2-(phenylselanyl)acetate (**1**) (2.65 g, 79%) as a yellow oil. IR (KBr, cm^{-1}) 1757 (CO); ^{1}H-NMR (500 MHz, $CDCl_3$) δ 1.17 (3H, t, J=7 Hz, Me), 4.08—4.13 (2H, m, OCH_2), 6.38 (1H, d, J=52 Hz, CHF), 7.32—7.41 (3H, m, ArH), 7.65—7.67 (2H, m, ArH); ^{19}F-NMR (470.5 MHz, $CDCl_3$) δ:−88.85 (1F, d, J=51 Hz); MS m/z 262 (M^+). *Anal.* Calcd for $C_{10}H_{11}FO_2Se$: C, 45.99; H, 4.25. Found: C, 45.97; H, 4.22.

Ethyl 2-Fluoro-2-(phenylsulfanyl)acetate (2) Triethylamine (7.20 g, 71.2 mmol) was added to a toluene (80.0 ml) solution of thiophenol (4.31 g, 39.1 mmol) and ethyl 2-chloro-2-fluoroacetate (5.00 g, 35.6 mmol). The reaction mixture was stirred for 40 min and then refluxed for 10 min. The cooled mixture was poured into water (100 ml). The organic layer was separated and aqueous layer was extracted with ether. The combined organic layer was dried over $MgSO_4$. The work-up procedure afforded **2** (4.61 g, 55%) as a yellow oil. IR (KBr, cm^{-1}) 3061, 2984, 2362, 2355, 1757, 1475, 1393, 1370, 1324, 1271, 1252, 1186, 1044, 1025, 948, 859, 813, 749, 691; ^{1}H-NMR (500 MHz, $CDCl_3$) δ: 1.19 (3H, t, J=7 Hz, Me), 4.15 (2H, q, J=7 Hz, OCH_2), 6.07 (1H, d, J=51 Hz, CHF), 7.34—7.39 (3H, m, ArH), 7.55—7.59 (2H, m, ArH); ^{19}F-NMR (470.5 MHz, $CDCl_3$) δ: −80.7 (1F, d, J=51 Hz); MS m/z 214 (M^+). *Anal.* Calcd for $C_{10}H_{11}FO_2S$: C, 56.06; H, 5.18. Found: C, 55.88; H, 5.02.

Preparation of 2-Fluoro-2-(phenylselanyl)acetamide (3) To EtOH (30.0 ml) solution of ethyl 2-fluoro-2-(phenylselanyl)acetate (**1**) (3.0 g, 11.5 mmol) was added aqueous 30% NH_3 (30.0 ml) at room temperature. The mixture was stirred for 15 min and poured into water (200 ml). The organic layer was separated and the aqueous layer was extracted with ether. The combined organic layer was dried over $MgSO_4$. The solvent was removed under reduced pressure. The residue was washed with *n*-hexane to form the white powders. The powders were filtrated to give the almost pure **3** (2.34 g, 88%). mp 87—89 °C (from CH_2Cl_2–*n*-hexane), IR (KBr, cm^{-1}) 3179 (NH), 1646 (CO), 1185 (NH); ^{1}H-NMR (500 MHz, $CDCl_3$) δ: 6.02 (1H, br s, NH_2), 6.19 (1H, br s, NH_2), 6.42 (1H, d, J=54 Hz, CHF), 7.26—7.70 (5H, m, ArH); ^{19}F-NMR (470.5 MHz, $CDCl_3$) δ: −84.3 (1F, d, J=53 Hz); MS m/z 233 (M^+). *Anal.* Calcd for C_8H_8NFOSe: C, 41.40; H, 3.47; N, 6.03. Found: C, 41.26; H, 3.46; N, 5.87.

2-Fluoro-2-(phenylsulfanyl)acetamide (4) To EtOH (30.0 ml) solution of ethyl 2-fluoro-2-(phenylsulfanyl)acetate (3.00 g, 14.0 mmol) was added aqueous NH_3 solution (30.0 ml) at room temperature. The mixture was stirred for 1 h. The usual work-up afforded 2-fluoro-2-(phenylsulfanyl)acetamide (**6**) (2.16 g, 83%) as white needles (from CH_2Cl_2–*n*-hexane). mp 86—87 °C, IR (KBr, cm^{-1}) 3179 (NH), 1673 (CO), 1155 (CN); ^{1}H-NMR (500 MHz, $CDCl_3$) δ: 6.09 (1H, br d, J=53 Hz, CHF), 6.11 (2H, s, NH_2), 7.38—7.40 (3H, m, ArH), 7.58—7.61 (2H, m, ArH); ^{19}F-NMR (470.5 MHz, $CDCl_3$) δ: −76.5 (1F, d, J=53 Hz); MS m/z 185 (M^+). *Anal.* Calcd for C_8H_8FNOS: C, 51.88; H, 4.35; N, 7.56. Found: C, 51.58; H, 4.33; N, 7.53.

Preparation of 2-Fluoro-2-(phenylselanyl)acetonitrile (5) Under an Ar atmosphere, a benzene (3.0 ml) solution of **3** (1.16 g, 5.00 mmol) was added to a benzene solution of PPSE (prepared from phosphorous pentoxide (5.00 g, 35.2 mmol) and hexamethyl disiloxane (15.0 ml))[8] at room temperature. The mixture was refluxed for 12 h and poured into water (100 ml). The organic layer was separated and the aqueous layer was extracted with ether. The combined organic layer was dried over $MgSO_4$. The solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel eluting with EtOAc–*n*-hexane (1 : 10) to give **5** (0.82 g, 77%) as a yellow oil. IR (KBr, cm^{-1}) 2246 (CN); ^{1}H-NMR (500 MHz, $CDCl_3$) δ: 6.44 (1H, d, J=50 Hz, CHF), 7.37—7.70 (5H, m, ArH); ^{19}F-NMR (470.5 MHz, $CDCl_3$) δ: −86.77 (1F, d, J=49 Hz); MS m/z 215 (M^+). *Anal.* Calcd for C_8H_6NFSe: C, 44.88; H, 2.82; N, 6.54. Found: C, 44.68; H, 2.78; N, 6.35.

Scandium Triflate-Catalyzed Allylation of Ethyl 2-Fluoro-2-(phenylselanyl)acetate (1), Typical Procedure Under an Ar atmosphere, scandium triflate (9.4 mg, 0.02 mmol) was added to a CH_2Cl_2 (1.0 ml) solution of **1** (0.10 g, 0.38 mmol) and allyltrimethylsilane (0.13 g, 1.15 mmol) at room temperature. The reaction mixture was stirred for 1.5 h and poured into a saturated $NaHCO_3$. The organic layer was separated and the aqueous layer was extracted with $CHCl_3$. The combined organic layer was dried over $MgSO_4$. The solvent was removed under reduced pressure. The residue was purified by preparative TLC on silica gel eluting with EtOAc–*n*-hexane (1 : 20) to give ethyl 2-(phenylselanyl)pent-4-enoate (**6a**) (94 mg, 87%) as a pale yellow oil. IR (KBr, cm^{-1}) 3074, 2980, 2935, 2364, 2344, 1727, 1578, 1476, 1437, 1369, 1338, 1301, 1272, 1247, 1232, 1185, 1139, 1022, 998, 920, 856, 794, 741; ^{1}H-NMR (500 MHz, $CDCl_3$) δ: 1.16 (3H, t, J=7 Hz, Me), 2.49—2.55 (1H, m, CH_2), 2.63—2.69 (1H, m, CH_2), 3.66 (1H, dd, J= 6, 9 Hz, SeCH), 4.08 (2H, q, J=7 Hz, OCH_2), 5.07—5.12 (2H, m, olefinic H), 5.75—5.83 (1H, m, olefinic H), 7.26—7.35 (3H, m, ArH), 7.60 (2H, d, J=7 Hz, ArH); ^{13}C-NMR (100 MHz, $CDCl_3$) δ: 14.11 (q), 36.06 (t), 42.59 (d), 61.06 (t), 117.70 (t), 127.80 (s), 128.62 (d), 129.08 (d×2), 134.78 (d), 135.84 (d×2), 172.51 (s); high-resolution mass calcd for $C_{13}H_{16}O_2Se$: 284.0315, found m/z 284.0310.

Reaction of 1 with 1-Phenyl-1-(trimethylsilyloxy)ethylene The reaction of **1** (0.10 g, 0.38 mmol), 1-phenyl-1-(trimethylsilyloxy)ethylene (90 mg, 0.38 mmol) and scandium triflate (11 mg, 0.02 mmol) in CH_2Cl_2 (1.0 ml) at room temperature afforded ethyl 3-benzoyl-2-(phenylselanyl)propionate (**6b**) (0.11 g, 78%) as a pale yellow oil. IR (KBr, cm^{-1}) 3058, 2980, 2924, 2362, 1725, 1685, 1596, 1579, 1476, 1448, 1394, 1371, 1352, 1326, 1299, 1214, 1160, 1096, 1023, 1000, 986, 858, 742; ^{1}H-NMR (500 MHz, $CDCl_3$) δ: 1.18 (3H, t, J=7 Hz, Me), 3.42 (1H, dd, J=4, 18 Hz, $COCH_2$), 3.70 (1H, dd, J=10, 18 Hz, $COCH_2$), 4.12 (2H, q, J=7 Hz, OCH_2), 4.21 (1H, dd, J=4, 10 Hz, CHSe), 7.30—7.66 (8H, m, ArH), 7.89—7.98 (2H, m, ArH); ^{13}C-NMR (100 MHz, $CDCl_3$) δ: 13.94 (q), 37.08 (d), 41.29 (t), 61.21 (t), 127.29 (d), 128.05 (d×2), 128.62 (d×2), 128.81 (d), 129.11 (d×2), 133.43 (d), 135.91 (d×2), 136.18 (s), 172.54 (s), 192.24 (s); MS m/z 362 (M^+). *Anal.* Calcd for $C_{18}H_{18}O_3Se$: C, 59.84; H, 5.02. Found: C, 60.03; H, 5.11.

Reaction of 2 with Allyltrimethylsilane Reaction of **2** (0.10 g, 0.47 mmol), allyltrimethylsilane (0.16 g, 1.40 mmol) and scandium triflate (11 mg, 0.02 mmol) in 1,2-dichloroethane (1.0 ml) at room temperature afforded ethyl 2-(phenylsulfanyl)pent-4-enoate (**7a**) (96 mg, 86%) as a pale

yellow oil. IR (KBr, cm^{-1}) 1731, 1438, 1368, 1232, 1155, 1024, 921, 748, 692; ^{1}H-NMR (500 MHz, $CDCl_3$) δ: 1.17 (3H, t, J=7 Hz, Me), 2.51—2.63 (2H, m, CH_2), 3.68—3.72 (1H, m, SCH), 4.11 (2H, q, J=7 Hz, OCH_2), 5.08—5.16 (2H, m, olefinic H), 5.78—5.85 (1H, m, olefinic H), 7.26—7.32 (3H, m, ArH), 7.46—7.48 (2H, m, ArH); ^{13}C-NMR (100 MHz, $CDCl_3$) δ: 14.06 (q), 35.83 (t), 50.25 (d), 61.13 (t), 118.01 (t), 127.23 (s), 128.01 (d), 128.91 (d×2), 133.08 (d×2), 133.86 (d), 171.62 (s); MS m/z 195 (M^+-allyl). *Anal.* Calcd for $C_{13}H_{16}O_2S$: C, 66.07; H, 6.82. Found: C, 65.95; H, 6.77.

Reaction of 2 with 1-Phenyl-1-(trimethylsilyloxy)ethylene Reaction of **2** (0.10 g, 0.47 mmol), 1-phenyl-1-(trimethylsilyloxy)ethylene (0.18 g, 0.93 mmol) and scandium triflate (11 mg, 0.02 mmol) in 1,2-dichloroethane (1.0 ml) at 0 °C afforded ethyl 3-benzoyl-2-(phenylsulfanyl)propionate (**7b**) (0.13 g, 89%) as a yellow oil. IR (KBr, cm^{-1}) 3059, 2980, 2360, 1731, 1684, 1596, 1580, 1473, 1448, 1398, 1328, 1241, 1213, 1159, 1094, 1024, 1001, 949, 857, 754, 690; ^{1}H-NMR (500 MHz, $CDCl_3$) δ: 1.15 (3H, t, J=7 Hz, Me), 3.36 (1H, dd, J=4, 18 Hz, $COCH_2$), 3.68 (1H, dd, J=10, 18 Hz, $COCH_2$), 4.12 (2H, q, J=7 Hz, OCH_2), 4.24 (1H, dd, J=4, 10 Hz, SCH), 7.30—7.54 (8H, m, ArH), 7.89—7.91 (2H, m, ArH); ^{13}C-NMR (100 MHz, $CDCl_3$) δ: 13.77 (q), 40.68 (t), 45.03 (d), 61.10 (t), 127.85 (d×2), 128.07 (d), 128.26 (d×2), 128.43 (d×2), 132.27 (s), 133.27 (d), 133.45 (d×2), 135.89 (s), 171.35 (s), 196.54 (s); MS m/z 314 (M^+). *Anal.* Calcd for $C_{18}H_{18}O_3S$: C, 68.76; H, 5.77. Found: C, 68.58; H, 5.72.

Reaction of 2 with Phenylsulfanyltrimethylsilane Reaction of **2** (0.10 g, 0.47 mmol), phenylsulfanyltrimethylsilane (0.17 g, 0.93 mmol) and scandium triflate (11 mg, 0.02 mmol) in 1,2-dichloroethane (1.0 ml) at room temperature afforded 2,2-bis(phenylsulfanyl)acetate (**7c**) (0.14 g, 95%) as a yellow oil. IR (KBr, cm^{-1}) 3437, 2358, 1731, 1714, 1633, 1471, 1439, 1364, 1280, 1141, 1026, 740; ^{1}H-NMR (500 MHz, $CDCl_3$) δ: 1.18 (3H, t, J=7 Hz, Me), 4.14 (2H, q, J=7 Hz, OCH_2), 4.84 (1H, s, SCH), 7.32—7.34 (6H, m, ArH), 7.48—7.50 (4H, m, ArH); ^{13}C-NMR (100 MHz, $CDCl_3$) δ: 13.93 (q), 58.30 (t), 62.10 (d), 128.62 (d×2), 129.04 (d×4), 132.78 (s×2), 133.37 (d×4), 171.43 (s); MS m/z 304 (M^+). *Anal.* Calcd for $C_{16}H_{16}O_2S$: C, 63.13; H, 5.30. Found: C, 62.94; H, 5.27.

Reaction of 4 with Allyltrimethylsilane Under an Ar atmosphere, scandium triflate (13 mg, 0.03 mmol) was added to a nitromethane (0.50 ml) solution of 2-fluoro-2-(phenylsulfanyl)acetamide (**4**) (0.10 g, 0.54 mmol) and allyltrimethylsilane (0.31 g, 2.70 mmol). The usual work-up afforded 2-(phenylsulfanyl)pent-4-enamide (**8a**) (92 mg, 82%) as pale yellow powders. mp 80—81 °C (from CH_2Cl_2–*n*-hexane), IR (KBr, cm^{-1}) 3381 (NH), 3186 (NH), 1654 (CO), 1157 (C–N); ^{1}H-NMR (500 MHz, $CDCl_3$) δ: 2.52—2.58 (1H, m, CH_2), 2.67—2.72 (1H, m, CH_2), 3.69 (1H, t, J=7 Hz, CH), 5.11—5.18 (2H, m, olefinic H), 5.81—5.89 (1H, m, olefinic H), 6.52 (1H, br s, NH), 6.54 (1H, br s, NH), 7.21—7.47 (5H, m, ArH); ^{13}C-NMR (100 MHz, $CDCl_3$) δ: 36.21 (t), 51.79 (d), 118.11 (t), 127.31 (d), 129.07 (d×2), 130.69 (d×2), 133.51 (s), 133.71 (d), 173.84 (s); MS m/z 207 (M^+). *Anal.* Calcd for $C_{11}H_{13}NOS$: C, 63.74; H, 6.32; N, 6.76. Found: C, 63.57; H, 6.07; N, 6.68.

Reaction of 4 with 1-Phenyl-1-(trimethylsilyloxy)ethylene Scandium triflate (13 mg, 0.02 mmol) was added to a nitromethane (1.0 ml) solution of **4** (0.10 g, 0.54 mmol) and 1-phenyl-1-(trimethylsilyloxy)ethylene (0.31 g, 1.62 mmol) at room temperature. The reaction mixture was stirred for 4 h. The usual work-up afforded 3-benzoyl-2-(phenylsulfanyl)propionamide (**8b**) (46 mg, 30%) as yellow powders. mp 154—156 °C (from CH_2Cl_2–*n*-hexane), IR (KBr, cm^{-1}) 3430 (NH), 1680 (CO), 1182 (C–N); ^{1}H-NMR (500 MHz, $CDCl_3$) δ: 3.42 (1H, dd, J=5, 18 Hz, CH2), 3.79 (1H, dd, J=7, 18 Hz, CH_2), 4.27 (1H, dd, J=5, 7 Hz, CH), 5.85 (1H, br s, NH), 6.39 (1H, br s, NH), 7.29—7.36 (3H, m, ArH), 7.44—7.59 (5H, m, ArH), 7.93—7.95 (2H, m, ArH); ^{13}C-NMR (100 MHz, $CDCl_3$) δ: 40.78 (t), 46.71 (d), 128.15 (d×2), 128.27 (d), 128.64 (d×2), 129.36 (d×2), 132.44 (d×2), 133.15 (s), 133.50 (d), 136.20 (s), 173.01 (s), 197.08 (s); MS m/z 285 (M^+). *Anal.* Calcd for $C_{16}H_{15}NO_2S$: C, 67.34; H, 5.30; N, 4.91. Found: C, 67.14; H, 5.28; N, 5.28.

Reaction of 2-Fluoro-2-(phenylselanyl)acetamide (3) with Allyltrimethylsilane Scandium triflate (11 mg, 0.02 mmol) was added to a nitromethane (1.0 ml) solution of **3** (0.10 g, 0.43 mmol) and allyltrimethylsilane (0.25 g, 2.15 mmol) at room temperature. The reaction mixture was refluxed for 12 h. The usual work-up afforded 2-(phenylselanyl)pent-4-enamide (**8c**) (89 mg, 82%) as pale yellow powders. mp 66—67 °C (from CH_2Cl_2–*n*-hexane), IR (KBr, cm^{-1}) 1641 (CO), 1170 (C–N); ^{1}H-NMR (500 MHz, $CDCl_3$) δ: 2.52—2.57 (1H, m, CH_2), 2.69—2.74 (1H, m, CH_2), 3.62 (1H, t, J=7 Hz, CH), 5.08—5.15 (2H, m, olefinic H), 5.78—5.87 (1H, m, olefinic H), 5.97 (1H, br s, NH), 6.24 (1H, br s, NH), 7.27—7.33 (3H, m, ArH), 7.58 (2H, dd, J=1, 2 Hz, ArH); ^{13}C-NMR (100 MHz, $CDCl_3$) δ: 36.21 (t), 45.33 (d), 117.72 (t), 127.91 (s), 128.36 (d), 129.22 (d×2), 134.67 (d), 134.83 (d×2), 174.18 (s); MS m/z 255 (M^+). *Anal.* Calcd for $C_{11}H_{13}NOSe$: C, 51.98; H, 5.16; N, 5.51. Found: C, 51.77; H, 4.86; N, 5.52.

Scandium Triflate-Catalyzed Reaction of 2-Fluoro-2-(phenylselanyl) acetonitrile (5) with 1-Phenyl-1-(trimethylsilyloxy)ethylene Under an Ar atmosphere, scandium triflate (12.0 mg, 0.02 mmol) was added to a 1,2-dichloroethane (1.0 ml) solution of 2-fluoro-2-(phenylselanyl)acetonitrile (**5**) (0.10 g, 0.47 mmol) and 1-phenyl-1-(trimethylsilyloxy)ethylene (0.27 g, 1.40 mmol) at 0 °C. The reaction mixture was stirred for 20 min at room temperature and then poured into water. The usual work-up afforded 3-benzoyl-2-(phenylselanyl)propionamide (**9a**) (0.111 g, 75%) as a yellow oil. IR (KBr, cm^{-1}) 2234 (CN), 1680 (CO); ^{1}H-NMR (500 MHz, $CDCl_3$) δ: 3.54—3.58 (2H, m, CH_2), 4.25 (1H, t, J=7 Hz, CH), 7.35—7.89 (10H, m, ArH); ^{13}C-NMR (100 MHz, $CDCl_3$) δ: 19.55 (d), 41.52 (t), 119.67 (s), 125.67 (s), 127.98 (d×2), 128.76 (d×2), 129.53 (d×2), 129.82 (d), 133.92 (d), 135.37 (s), 136.53 (d×2), 194.16 (s); MS m/z 315 (M^+). *Anal.* Calcd for $C_{16}H_{13}NOSe$: C, 61.15; H, 4.17; N, 4.46. Found: C, 61.45; H, 4.20; N, 4.40.

Reaction of 2-Fluoro-2-(phenylselanyl)acetonitrile with 2-Methyl-1-(trimethylsilyloxy)prop-1-ene Reaction of 2-fluoro-2-(phenylselanyl)acetonitrile (**5**) (0.10 g, 0.47 mmol), 2-methyl-1-(trimethylsilyloxy)prop-1-ene (0.20 g, 1.40 mmol) and scandium triflate (12 mg, 0.02 mmol) at room temperature afforded 3-formyl-3-methyl-2-(phenylselanyl)butyronitrile (**9b**) (0.10 g, 81%) as a yellow oil. IR (KBr, cm^{-1}) 2971, 2932, 2232 (CN), 1727 (CO); ^{1}H-NMR (500 MHz, $CDCl_3$) δ: 1.33 (3H, s, Me), 1.39 (3H, s, Me), 3.83 (1H, s, CH), 7.26—7.73 (5H, m, ArH), 9.48 (1H, s, CHO); high resolution mass calcd for $C_{12}H_{13}NOSe$: 267.0162, found m/z 267.0047. The compound **9b** was easily oxidized to the corresponding carboxylic acid. (*Anal.* Calcd for $C_{12}H_{13}NO_2Se$: C, 51.07; H, 4.64; N, 4.96. Found: C, 50.57; H, 4.57; N, 4.62.)

Reaction of 5 with 3,3-Dimethyl-2-(trimethylsilyloxy)but-1-ene Reaction of **5** (0.10 g, 0.47 mmol), 3,3-dimethyl-2-(trimethylsilyloxy)but-1-ene (0.24 g, 1.40 mmol) and scandium triflate (12 mg, 0.02 mmol) in CH_2Cl_2 (1.0 ml) afforded 3-pivaloyl-2-(phenylselanyl)propionitrile (**9c**) (0.12 g, 85%) as a pale yellow oil. IR (KBr, cm^{-1}) 2234 (CN), 1708 (CO); ^{1}H-NMR (500 MHz, $CDCl_3$) δ: 1.19 (9H, s, Me×3), 3.08—3.10 (2H, m, CH_2), 4.10 (1H, t, J=7 Hz, CH), 7.39—7.74 (5H, m, ArH); ^{13}C-NMR (100 MHz, $CDCl_3$) δ: 19.76 (d), 26.07 (q×3), 39.99 (s), 43.94 (t), 119.78 (s), 125.93 (s), 129.58 (d×2), 129.81 (d), 136.38 (d×2), 209.92 (s); MS m/z 295 (M^+). *Anal.* Calcd for $C_{14}H_{17}NOSe$: C, 57.15; H, 5.82; N, 4.76. Found: C, 56.88; H, 5.78; N, 4.73.

Reaction of 5 with Anisole Reaction of **5** (0.10 g, 0.47 mmol), anisole (0.15 g, 1.40 mmol) and scandium triflate (23 mg, 0.05 mmol) in 1,2-dichloroethane (1.0 ml) afforded 2-(*p*-methoxyphenyl)-2-(phenylselanyl)acetonitrile (**9d**) (60.0 mg, 43%) as a yellow oil. IR (KBr, cm^{-1}) 2231 (CN), 1251; ^{1}H-NMR (500 MHz, $CDCl_3$) δ: 3.79 (3H, s, Me), 4.92 (1H, s, CH), 6.82—7.21 (4H, m, ArH), 7.31—7.59 (5H, m, ArH); ^{13}C-NMR (100 MHz, $CDCl_3$) δ: 29.27 (d), 55.33 (q), 114.27 (d×2), 118.81 (s), 124.96 (s), 126.83 (s), 128.86 (d×2), 129.34 (d×2), 129.79 (d), 136.76 (d×2), 159.73 (s); MS m/z 303 (M^+). *Anal.* Calcd for $C_{15}H_{13}NOSe$: C, 59.61; H, 4.34; N, 4.63. Found: C, 59.92; H, 4.48; N, 4.65.

Reaction of 5 with Toluene Reaction of **5** (0.10 g, 0.47 mmol), toluene (1.0 ml) and scandium triflate (12.0 mg, 0.02 mmol) in 1,2-dichloroethane (1.0 ml) afforded 2-(*p*-tolyl)- and 2-(*o*-tolyl)-2-phenylselanylacetonitrile (**9e**) (0.11 g, 81%).

9e: IR (KBr, cm^{-1}) 2234 (CN); ^{1}H-NMR (500 MHz, $CDCl_3$) δ: 2.33 (s, *p*-Me), 2.42 (s, *o*-Me), 4.91 (s, *p*-CH), 4.94 (s, *o*-Me), 7.07—7.25 (m, ArH), 7.30—7.44 (m, ArH), 7.57—7.58 (m, ArH); high-resolution mass calcd for $C_{15}H_{13}NSe$: 287.0210, found m/z 287.0183.

Preparation of Ethyl 2-Chloro-2-(phenylselanyl)acetate (10) Scandium triflate (47 mg, 0.01 mmol) was added to a nitromethane (5.0 ml) solution of **1** (0.50 g, 1.90 mmol) and chlorotrimethylsilane (0.62 g, 5.7 mmol) at room temperature. The mixture was refluxed for 5 min and poured into a sat. $NaHCO_3$ (50 ml) solution. The organic layer was separated and the aqueous layer was extracted with ether. The combined organic layer was dried over $MgSO_4$. The solvent was removed under reduced pressure. The residue was purified by the preparative TLC on silica gel eluting with EtOAc–*n*-hexane (1 : 20) to give **10** (0.53 g, quant.) as a pale yellow oil. IR (KBr, cm^{-1}) 1748 (CO), 1476, 1439, 1367, 1273, 1173, 1134, 1023, 866, 788, 741, 690; ^{1}H-NMR (500 MHz, $CDCl_3$) δ: 1.23 (3H, t, J=7 Hz, Me), 4.17 (2H, q, J=7 Hz, OCH_2), 5.52 (1H, s, CHCl), 7.35—7.37 (2H, m, ArH), 7.39—7.42 (1H, m, ArH), 7.67—7.70 (2H, m, ArH); ^{13}C-NMR (100 MHz, $CDCl_3$) δ: 13.84 (q), 53.04 (d), 62.62 (t), 126.72 (s), 129.26 (d×2), 134.91 (d), 135.96 (d×2), 167.04 (s); MS m/z 278 (M^+). *Anal.* Calcd for $C_{10}H_{11}ClO_2Se$: C, 43.27; H, 3.99. Found: C, 43.12; H, 3.89.

2-Chloro-2-(phenylselanyl)acetamide (11) Yield 83%, white needles,

mp 88 °C (from CH_2Cl_2–*n*-hexane), IR (KBr, cm^{-1}) 3333 (NH), 3166 (NH), 1666 (CO), 1630, 1577, 1478, 1436, 1229, 1163, 1071, 1021, 776, 732, 687, 632; ^{1}H-NMR (100 MHz, $CDCl_3$) δ: 5.56 (1H, s, CHCl), 6.25 (1H, br s, NH), 6.63 (1H, br s, NH), 7.27—7.40 (3H, m, ArH), 7.70—7.72 (2H, m, ArH); ^{13}C-NMR (100 MHz, $CDCl_3$) δ: 55.20 (d), 126.21 (s), 129.27 (d×2), 129.67 (d), 136.35 (d×2), 169.26 (s); MS *m*/*z* 249 (M^+). *Anal.* Calcd for $C_8H_8ClNOSe$: C, 38.66; H, 3.24; N, 5.64. Found: C, 38.47; H, 3.17; N, 5.62.

Ethyl 2-Bromo-2-(phenylselanyl)acetate (12) Yield 88%, a yellow oil, IR (KBr, cm^{-1}) 2982, 1737 (CO), 1577, 1476, 1439, 1367, 1258, 1136, 1022, 862, 779, 742, 690566, 468; ^{1}H-NMR (500 MHz, $CDCl_3$) δ: 1.22 (3H, t, *J*=7 Hz, Me), 4.16 (2H, q, *J*=7 Hz, OCH_2), 5.43 (1H, s, CHBr), 7.33—7.40 (3H, m, ArH), 7.65—7.66 (2H, m, ArH); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 13.65 (q), 39.64 (d), 62.49 (t), 127.48 (s), 129.13 (d×2), 129.27 (d), 135.19 (d×2), 166.68 (s); high-resolution mass calcd for $C_{10}H_{11}BrO_2Se$: 321.9153, found *m*/*z* 321.9180.

2-Bromo-2-(phenylselanyl)acetamide (13) Yield 64%, white needles, mp 130 °C (from CH_2Cl_2–*n*-hexane), IR (KBr, cm^{-1}) 3380 (NH), 3176 (NH), 1656 (CO), 1475, 1438, 1411, 1189, 1132, 1095, 1022, 1000, 773, 743, 690, 620, 539; ^{1}H-NMR (500 MHz, $CDCl_3$) δ: 5.46 (1H, CHBr), 5.82 (1H, br s, NH), 6.12 (1H, br s, NH), 7.38—7.43 (3H, m, ArH), 7.71 (2H, br s, ArH); ^{13}C-NMR (100 MHz, $CDCl_3$) δ: 42.08 (d), 127.39 (s), 129.43 (d×2), 129.76 (d), 135.89 (d×2), 168.60 (s); MS *m*/*z* 294 (M^+). *Anal.* Calcd for $C_8H_8BrNOSe$: C, 32.79; H, 2.75; N, 4.78. Found: C, 32.60; H, 2.69; N, 4.80.

Relative Reactivities of α-Fluoro-, α-Chloro- and α-Bromo-Ethyl Acetaes 1, 10, 12 and Acetamides 3, 11, 13, General Experimental Procedure Scandium triflate (5 mg, 0.01 mmol) was added to a nitromethane (0.50 ml) solution of ethyl 2-fluoro-2-(phenylselanyl)acetate (**1**) (50.0 mg, 0.19 mmol) and allyltrimethylsilane (0.11 g, 0.96 mmol) at room temperature. The reaction mixture was heated under a reflux condition for 5 min and poured into a sat. $NaHCO_3$ (50.0 ml) solution. The usual work-up afforded ethyl 2-(phenylselanyl)pent-4-enoate (**6a**) (54 mg, quant.)

Preparation of Ethyl 4-(Hydroxymethyl)-2-(phenylsulfanyl)pent-4-enoate (15) Scandium triflate (22 mg, 0.047 mmol) was added to a 1,2-dichloroethane (1.0 ml) solution of ethyl 2-fluoro-2-(phenylsulfanyl)acetate (**2**) (0.10 g, 0.47 mmol) and *O*-trimethylsilyl-2-(trimethylsilylmethyl)prop-2-en-1-ol (0.30 g, 1.40 mmol) at 0 °C. The reaction mixture was stirred for 1 h at room temperature. The usual work-up afforded title compound **15** (93 mg, 71%) as a pale yellow oil. IR (KBr, cm^{-1}) 3438 (OH), 1731 (CO), 1654, 1538, 1473, 1440, 1370, 1332, 1301, 1263, 1174, 1155, 1025, 908, 858, 750, 692; ^{1}H-NMR (500 MHz, $CDCl_3$) δ: 1.19 (3H, t, *J*=7 Hz, Me), 2.11 (1H, br s, OH), 2.59 (1H, dd, *J*=6, 15 Hz, CH_2), 2.73 (1H, dd, *J*=9, 15 Hz, CH_2), 3.93 (1H, dd, *J*=6, 10 Hz, CHS), 4.12 (2H, s, CH_2), 4.13 (2H, q, *J*=7 Hz, OCH_2), 4.99 (1H, d, *J*=1 Hz, olefinic H), 5.17 (1H, s, olefinic H), 7.31—7.35 (3H, m, ArH), 7.50—7.58 (2H, m, ArH); ^{13}C-NMR (100 MHz, $CDCl_3$) δ: 14.01 (q), 34.94 (t), 49.09 (d), 61.06 (t), 65.31 (t), 112.34 (t), 128.00 (d), 128.89 (d×2), 133.05 (d×2), 133.19 (s), 144.40 (s), 171.74 (s); high-resolution mass calcd for $C_{14}H_{18}O_3S$: 266.0976, found *m*/*z* 266.0954.

Preparation of 5-Methylene-3-(phenylsulfanyl)tetrahydro-2-pyrone (17) Scandium triflate (13 mg, 0.027 mmol) was added to a 1,2-dichloroethane (1.0 ml) solution of **15** (75 mg, 0.266 mmol) at room temperature. The reaction mixture was refluxed for 4 h and then poured into a saturated $NaHCO_3$ (50 ml). The organic layer was separated and the aqueous layer was extracted with $CHCl_3$. The combined organic layer was dried over $MgSO_4$. The solvent was removed under reduced pressure. The residue was purified by the preparative TLC on silica gel eluting with EtOAc–*n*-hexane (1 : 5) to give **17** (30 mg, 51%) as a colorless oil. IR (KBr, cm^{-1}) 1739 (CO), 1481, 1438, 1374, 1302, 1249, 1223, 1143, 1055, 1025, 908, 742, 692; ^{1}H-NMR (500 MHz, $CDCl_3$) δ: 2.77 (1H, dd, *J*=6, 17 Hz, 4-H), 3.03 (1H, dd, *J*=6, 17 Hz, 4-H), 4.01 (1H, t, *J*=6 Hz, 3-H), 4.82 (1H, d, *J*=14 Hz, 6-H), 5.07 (1H, d, *J*=1 Hz, olefinic H), 5.08 (1H, d, *J*=14 Hz, 6-H), 5.13 (1H, t, *J*=1 Hz, olefinic H), 7.32—7.36 (3H, m, ArH), 7.53—7.54 (2H, m, ArH); ^{13}C-NMR (100 MHz, $CDCl_3$) δ: 33.17 (t), 46.26 (d), 71.53 (t), 113.18 (t), 128.53 (d), 129.21 (d×2), 132.21 (s), 133.25 (d×2), 135.65 (s), 169.10 (s); high-resolution mass calcd for $C_{12}H_{12}O_2S$: 220.0558, found *m*/*z* 220.0537.

Preparation of Ethyl 4-(Hydroxymethyl)-2-(phenylselanyl)pent-4-enoate (14) Scandium triflate (56 mg, 0.12 mmol) was added to a 1,2-dichloroethane (3.0 ml) solution of ethyl 2-fluoro-2-(phenylselanyl)acetate (**1**) (0.30 g, 1.14 mmol) and *O*-trimethylsilyl-2-(trimethylsilylmethyl)prop-2-en-1-ol (0.50 g, 2.30 mmol) at 0 °C. The reaction mixture was stirred for 30 min at room temperature. Tetrabutylammonium fluoride in THF (3 drops of 1 M) was added dropwise to the mixture. The whole was stirred for 1 h and poured into water (100 ml). The usual work-up afforded **14** (0.16 g, 43%) as a pale yellow oil. IR (KBr, cm^{-1}) 3449 (OH), 1725 (CO), 1476, 1439, 1370, 1302, 1260, 1159, 1022, 909, 742, 692; ^{1}H-NMR (500 MHz, $CDCl_3$) δ: 1.13 (3H, t, *J*=7 Hz, Me), 2.38 (1H, br s, OH), 2.55 (1H, dd, *J*=6, 15 Hz, 3-H), 2.71 (1H, dd, *J*=10, 15 Hz, 3-H), 3.85 (1H, dd, *J*=6, 10 Hz, 4-H), 4.02 (2H, s, 5-H), 4.05 (2H, q, *J*=7 Hz, OCH_2), 4.90 (1H, s, olefinic H), 5.09 (1H, s, olefinic H), 7.27—7.35 (3H, m, ArH), 7.59—7.61 (2H, m, ArH); ^{13}C-NMR (100 MHz, $CDCl_3$) δ: 13.84 (q), 34.93 (t), 41.20 (d), 60.98 (t), 65.53 (t), 112.26 (t), 127.51 (s), 128.53 (d), 128.92 (d×2), 135.64 (d×2), 145.66 (s), 172.69 (s); MS *m*/*z* 312 (M^+-H_2O). *Anal.* Calcd for $C_{14}H_{18}O_4Se$: C, 53.68; H, 5.79. Found: C, 53.83; H, 5.83.

Preparation of 5-Methylene-3-(phenylselanyl)tetrahydro-2-pyrone (16) Scandium triflate (13 mg, 0.027 mmol) was added to a 1,2-dichloroethane (1.0 ml) solution of **14** (85 mg, 0.258 mmol) at room temperature. The reaction mixture was refluxed for 12 h and then poured into a saturated $NaHCO_3$ (50 ml). The usual work-up afforded **16** (22 mg, 32%) as a yellow oil. IR (KBr, cm^{-1}) 3449, 1734 (CO), 1578, 1560, 1543, 1509, 1476, 1459, 1438, 1378, 1300, 1219, 1169, 1129, 1057, 741, 691; ^{1}H-NMR (500 MHz, $CDCl_3$) δ: 2.82 (1H, dd, *J*=5, 16 Hz, 4-H), 3.06 (1H, dd, *J*=6, 16 Hz, 4-H), 4.05 (1H, t, *J*=6 Hz, 3-H), 4.83 (1H, d, *J*=14 Hz, 6-H), 5.03 (1H, d, *J*=14 Hz, 6-H), 5.06 (1H, s, olefinic H), 5.12 (1H, s, olefinic H), 7.31—7.36 (3H, m, ArH), 7.65—7.66 (2H, m, ArH); ^{13}C-NMR (100 MHz, $CDCl_3$) δ: 33.83 (t), 38.56 (d), 71.71 (t), 113.07 (t), 127.49 (s), 128.84 (d), 129.32 (d×2), 135.38 (d×2), 135.66 (s), 169.84 (s); MS *m*/*z* 268 (M^+). *Anal.* Calcd for $C_{12}H_{12}O_2Se$: C, 53.94; H, 4.52. Found: C, 54.19; H, 4.75.

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